

Amines used for low temperature curing of PDMS-based gel-networks impact γ -irradiation outcome

Abstract

Four structurally different amines: 1,3-diamino-2-propanol (DAP), diethylenetriamine (DETA), tris(2-aminoethyl)amine (TAEA) and triethylenetetramine (TETA) were reacted with diglycidyl ether terminated poly(dimethylsiloxane), PDMS-DGE at relatively low temperature of 50 °C. Stable transparent networks with gel-like properties but without a liquid component, “gel networks” were obtained. Raman spectra revealed presence of residual epoxy-group absorptions in cured gel-networks but secondary amine absorption intensities in FTIR spectra were used for monitoring of the curing reaction extent. To assess their radiation stability gel-networks were gamma-irradiated to absorbed dose of 50 kGy. Even though contribution of amine segments to PDMS-based gel-networks is relatively small their structure significantly influenced the properties of studied PDMS-based gel-networks. The most important property of an amine was the ability to either form hydrogen bonds, or produce denser network like a triamine. However there were also significant differences in properties of gel-networks prepared with mutually similar diamines DETA and TETA that can be considered a dimer and a trimer of ethylenediamine. In the studied gel-networks there is a complex interaction of extent of initial curing that depended on the amine used and the resulting (dis)order that strongly influenced the outcome of irradiation. The temperature of an endothermic transition presumably caused by reversible gel-network collapse was observed in DSC thermograms of all the gel-networks. The temperature depended on the amine type and shifted to higher values on irradiation. Changes in most properties like residual gel content on extraction or AC electrical conductivity and its frequency dependence were more pronounced in gel-networks prepared with diamines DETA and TETA than in those prepared with amines capable of significant secondary valent interactions (DAP and TAEA). Radiation curing and/or crosslinking seem to have occurred only in TETA-cured gel-network and it was mostly due to lower extent of initial reaction. Since swelling of gel-networks increased it may be concluded that irradiation improved their properties.

Keywords

Polylsiloxane, aliphatic amines, ionizing radiation, DSC, vibrational spectroscopy, dielectric spectroscopy

1. INTRODUCTION

Polymer gels are generally defined as polymer-solvent system in which macromolecular three-dimensional network retains the solvent that is not chemically bound to the polymer (Rogovina et al., 2008; Yamauchi, 2001). However the term “gel” also describes other soft materials that keep their shape under the action of their own weight. Properties of the polymer gel may vary greatly depending on the polymer backbone and chosen solvent that can be present in large amounts. Polymer gels can be prepared by crosslinking monomers or oligomers with reactive terminal groups in a solvent or by swelling of a gel-network, a previously crosslinked polymer. Although

gel-networks do not contain a liquid component they exhibit most of gel properties. (Jones et al., 2009).

Poly(dimethylsiloxane), PDMS is often used as a polymeric backbone for various gels. It is the most common semi-inorganic polysiloxane polymer. (Mark, 2004). It is a versatile, non-toxic, environmentally friendly polymer with many excellent chemical, physical, and electrical properties so it's widely used for commercial, industrial and military purposes. PDMS is highly tissue equivalent so it's used for preparation of 3D polymer gel dosimeter (Deene et al., 2015). Gels are easily obtained by curing of PDMS oligomers terminated with reactive groups with appropriate reactants (Petrie, 2006). The rate of curing process can be controlled by temperature and/or by use of additional accelerating agents (e.g. alcohols). In general curing can be divided into room temperature and elevated-temperature curing. Room temperature curing often requires very reactive curing agents like aliphatic amines. Less shrinkage and internal stress resulting from thermal expansion differences, moderate strength, better heat and chemical resistance, good toughness are advantages of room temperature curing. Its downside is that it usually results in lower crosslink density (Petrie, 2006).

The aim of this research was to prepare low-temperature cured PDMS gel-networks with selected aliphatic amine curing agents and to determine if and how the amine type affects some of the properties of obtained gel-networks. For many purposes and for military use in particular it is important to assess the response of a material to ionizing radiation produced after bursts of nuclear weapons and radiological dispersal devices (RDD). Wide range of radiation induced processes occur on exposition to ionizing radiation that can either degrade (main chain scission) or crosslink polysiloxanes. Crosslinking mainly happens as a result of radicals formed by Si-C and C-H bond scission (Hill et al., 2001). Both processes occur simultaneously and their outcome depends on the side groups on polysiloxane chain and the irradiation conditions (Palsule et al., 2008; Djouani et al., 2014). These reactions can then influence various characteristics of an irradiated gel or gel-network like its thermomechanical properties what is particularly important since PDMS is an elastomer. Thus we irradiated the PDMS-based gel-networks that were cured at low temperature and compared their properties to those of non-irradiated ones.

2. MATERIALS AND METHODS

2.1. Preparation and irradiation of PDMS-based gel-networks

Gel-networks were prepared by reaction of PDMS-DGE with selected aliphatic amines as curing reagents: diamines 1,3-diamino-2-propanol (DAP), diethylenetriamine (DETA), triethylenetetramine (TETA) and a triamine tris(2-aminoethyl)amine (TAEA). Their structural formulas are shown in figure 1. PDMS-DGE with molecular weight of about 800 was purchased from Sigma Aldrich. Amines DAP and DETA from Alfa Aesar and TAEA and TETA from Acros Organics. All reagents were used as received. Each particular amine and PDMS-DGE were mixed in 1:1 stoichiometric ratio and the reaction was carried out for 144 hours at 50 °C.

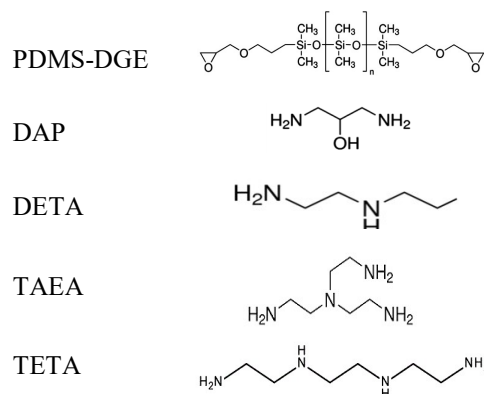


Fig. 1. Chemical structure of PDMS-DGE and selected aliphatic amine curing agents.

A part of each obtained gel-network was irradiated in the panoramic ^{60}Co γ -irradiator at a Laboratory for Radiation Chemistry and Dosimetry irradiation facility Ruđer Bošković Institute (RBI) in Zagreb, Croatia. The samples were exposed to dose of 50 kGy at a dose rate of 7.8 Gy/s, in ambient conditions. Prior to any characterization irradiated samples were kept in ambient conditions for at least five days.

Table 1. List of abbreviations used for reactants and samples

Abbreviation	Sample
PDMS-DGE	poly(dimethylsiloxane), diglycidyl ether terminated
DAP	1,3-diamino-2-propanol
DETA	diethylenetriamine
TAEA	triethylenetetramine
TETA	triamine tris(2-aminoethyl)amine
DAP-GN	DAP amine
DETA-GN	PDMS-DGE gel-network crosslinked with DETA amine
TAEA-GN	TAEA amine
TETA-GN	TETA amine

2.2. Characterization of non-irradiated and irradiated PDMS-based gel-networks

The ATR-FTIR spectra of amines, PDMS-DGE and prepared gel-networks were recorded using Bruker TENSOR II FTIR spectrophotometer equipped with A225/Q Platinum diamond ATR unit. Spectral range was 400 to 4000 cm^{-1} and 16 scans were recorded with resolution of 4 cm^{-1} . For each gel-network sample spectra were taken on at least four locations. OPUS software was used for spectra collection and SpectraGryph v1.2.12 software for further processing. All gel-networks spectra were normalized to 1258 cm^{-1} PDMS-DGE absorption.

For acquisition of Raman spectra a T64000 HORIBA JobinYvon Raman spectrometer operating in triple subtractive mode using a 90° macro chamber and equipped with a liquid nitrogen cooled CCD detector with 256 x 1024 pixels array was used. Liquid samples were injected in glass capillaries, while solid ones were positioned on a holder in front of the focusing lens. The entrance slit was 300 μm . Diode laser of the DPSS type with 532 nm wavelength produced by

Changchun New industries Optoelectronics Tech. served as an excitation source. The power at the sample was 4 mW. Time accumulation of spectra varied from 20 s to 30 s, with four repetitions to increase the signal to noise ratio. Spectral resolution was 0.6 cm⁻¹ per pixel. All spectra were obtained within spectral interval from 50 to 3800 cm⁻¹. LabSpec NGS software was used for spectra collection and SpectraGryph v1.2.12 software for further analysis.

For Soxhlet extraction *n*-hexane was chosen as the most suitable solvent for PDMS according to Brockmeyer et al., (2015). ACS reagent grade *n*-hexane was purchased from Honeywell and was used without any further purification. The non-irradiated and irradiated samples were extracted in Soxhlet apparatus for total of 48 hours. The temperature of the condensed hexane flushing the sample was measured using infrared thermometer (TFA 31.1134.06) and it was around 50 °C. After extraction samples were dried in vacuum dryer for 24 hours at 50 °C. Percentage of remaining mass was calculated using equation:

$$\% \text{ remaining mass} = \left(1 - \frac{m_0 - m_t}{m_t}\right) \cdot 100 \quad (1)$$

where m_0 presents sample mass before extraction and m_t sample mass after extraction and drying. Swelling was conducted in *n*-hexane (the same as was used for the Soxhlet extraction) at 23 °C using continuous method described by Liu et al. (2013). Samples were submerged in *n*-hexane and their mass was measured at selected intervals for at least 24 hours. Before each weighting the samples were wiped with paper tissue to remove external *n*-hexane on sample surface. The degree of swelling was calculated using equation:

$$\% \text{ swelling} = \frac{m_t - m_0}{m_0} \cdot 100 \quad (2)$$

where m_0 presents sample mass before swelling and m_t sample mass after swelling time t .

Dielectric spectra were recorded at room temperature (23 °C) on Novocontrol Technologies instrument with Alpha-A High Performance Frequency Analyzer, standard BDS1200 cell and brass electrodes. Samples were put in 3 mm high cylindrical Teflon holder with diameter of 5 mm and measured under AC voltage of 0.1 V, in frequency range from 1·10⁶ to 5·10⁻² Hz. The data were collected using Novocontrol system analysis software WinDETA v5.65.

DSC measurements were performed on Perkin Elmer Pyris Diamond DSC in nitrogen atmosphere. The gel-network samples were cut to weight of about 5 mg, put in 50 µl aluminum sample pan and crimped. For each sample two heating and cooling thermograms were recorded in the temperature range between -50 °C and 250 °C, at a rate of 20 °C /min. The data were collected and analyzed using Pyris software provided by Perkin Elmer.

3. RESULTS AND DISCUSSION

All the selected amines reacted with PDMS-DGE at 50 °C and produced transparent and firm gel-networks. Figure 2 shows two step addition reaction of primary amine with DGE (epoxy) group.

At low temperature curing is slower so heat distribution is even and resulting gel-networks are more uniform.

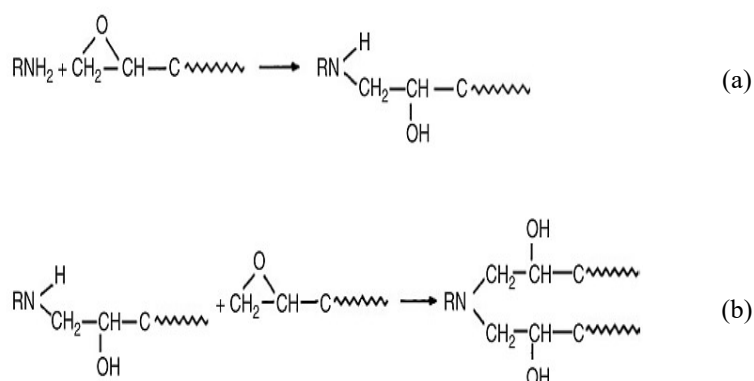


Fig. 2. Scheme of the reaction of the epoxy group with primary amine (Petrie, 2006).

Apparent firmness of gel-networks noticeably differed depending on the amine used for curing. The firmest was the one prepared using DAP, the shortest chain of selected aliphatic amines. That is likely a consequence of hydrogen bonding by hydroxy group of DAP. A triamine, TAEA that has six amine hydrogens available to reaction with DGE groups produced similarly firm gel-network. The ones obtained by reaction with diamines DETA and TETA that can be considered a dimer and a trimer of ethylenediamine were somewhat less firm.

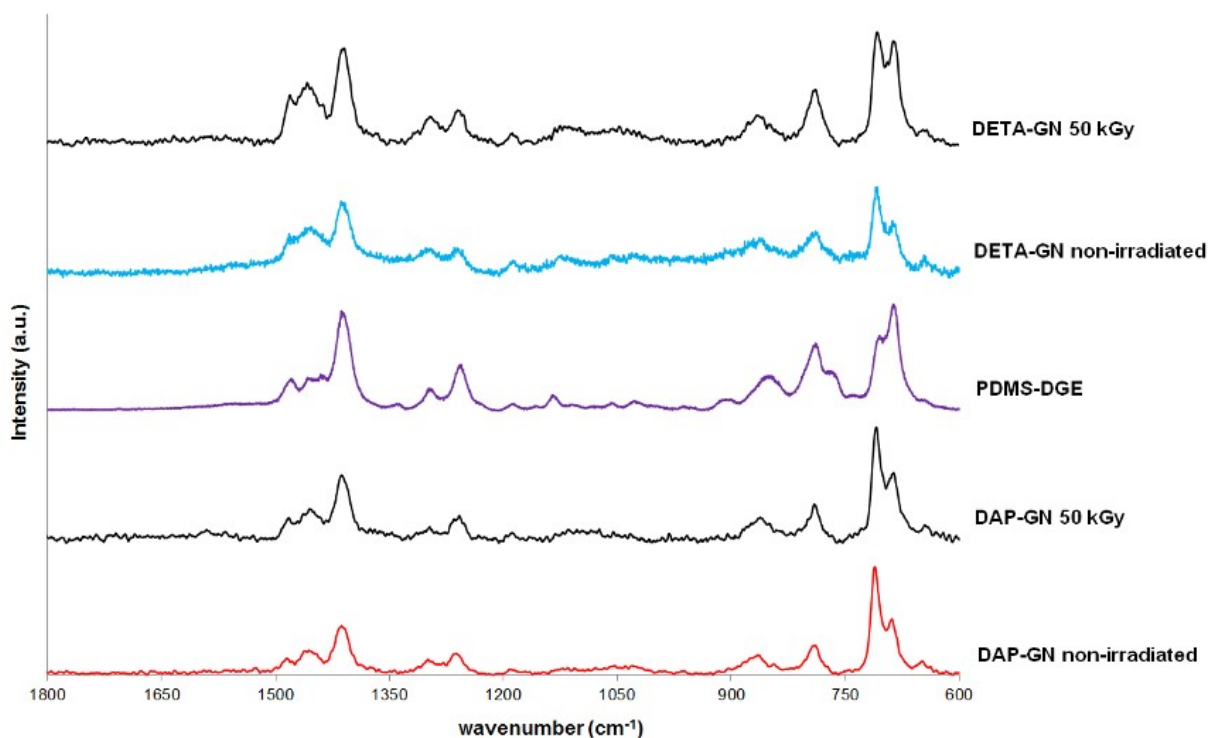


Fig. 3. Partial Raman spectra of non-irradiated DAP- and DETA-cured PDMS-DGE gel-networks and those irradiated to D = 50 kGy.

Because the low reaction temperature and the fact that PDMS molecule tend to coil, some of the end epoxy (DGE) groups must have remained inaccessible to reaction. In case of PDMS-DGE the irradiation will not only affect -Si-C- bonds but also the isopropanol segment formed on opening of the epoxy ring during curing process (Djouani et al., 2014). To detect unreacted end epoxy groups and to compare reaction extents spectroscopic analysis was performed.

Characteristic vibrational frequencies observed in ATR-FTIR and Raman spectra of studied gel-networks and the reactants used to prepare them are listed in Table 2. The most prominent infrared absorption of epoxy group (-C-O- stretching) at 1250 cm⁻¹ in spectra of pure PDMS-DGE overlapped with much stronger methyl group absorption at 1258 cm⁻¹ while 370 cm⁻¹ (ring deformation) absorption was outside measurement range of the FTIR instrument. The only epoxy ring absorption visible in ATR-FTIR spectra of pure PDMS-DGE was a low intensity peak at 910 cm⁻¹. That peak was absent in all of the spectra of the gel-networks whether non-irradiated or irradiated. Still, due to the weakness of initial absorption that is no proof that all the DGE groups have reacted. In Raman spectra of PDMS-DGE (Fig. 3, middle) epoxy absorption was observed at 1260 cm⁻¹. It was also present in Raman spectra of all the studied gel-networks but its intensity was much lower. That confirms the presumption that some DGE groups remained unreacted.

Table 2. Infrared and Raman absorptions observed in spectra of PDMS-based gel-networks and their assignments. (Cai et al., 2010; Socrates, 2001).

ATR-FTIR		Raman		Vibrational mode	
Wavenumber (cm ⁻¹)	Relative band strength	Wavenumber (cm ⁻¹)	Relative band strength	PDMS-DGE	amine
505	w	495	m	$\pi(\text{CH}_2)$ in glycidoxo, $\tau(\text{CH}_2)$ in propyl chain, $\delta(\text{C-H})$ in glycidoxo	$\delta(\text{CH}_2\text{-NH-CH}_2)$
687	m	686, sh	w	$\pi(\text{CH}_3)$	-
696	m	709	m		
791	vs	793	vw	$\rho(\text{CH}_3)$	$\rho(\text{CH}_2)$, $\pi(\text{NH}_2)$
-	-	864	m	$\nu(\text{Si-(CH}_3)_2)$	-
-	-	910	vw	$\nu(\text{C-O-C})$ in epoxy	-
1015	s	1017	vw	$\nu(\text{O-Si-O})$, $\pi(\text{CH}_2)$ in propyl chain	-
1075, sh	s	1053	vw	$\nu(\text{O-Si-O})$	-
-	-	1125	w	$\pi(\text{CH}_2)$ in epoxy, $\delta(\text{C-H})$	-
1250	s	1260	vw	$\nu(\text{-C-O-})$ in epoxy	-
1306	w	1300	vw	$\delta(\text{CH}_3)$	$\tau(\text{NH}_2)$
1410	w	1411	w	$\delta(\text{CH}_2)$ in epoxy, $\delta(\text{C-H})$ in epoxy, $\pi(\text{CH}_2)$ in propyl chain, $\pi(\text{CH}_2)$ in glycidoxo	-
1570	w	-	-	-	$\delta(\text{NH})$
1596	w	-	-	-	$\delta(\text{NH}_2)$

3437	w	-	-	-	v(N-H)
3200-3600	w	3200-3600	vw	v(O-H)	-

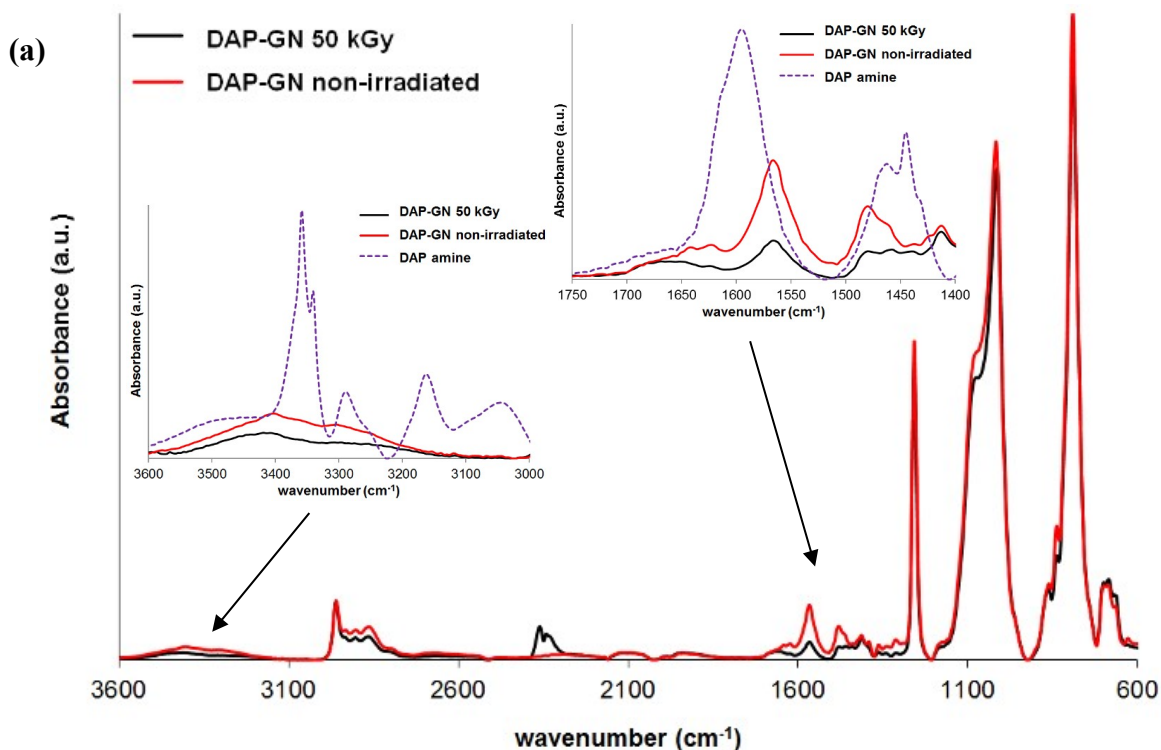
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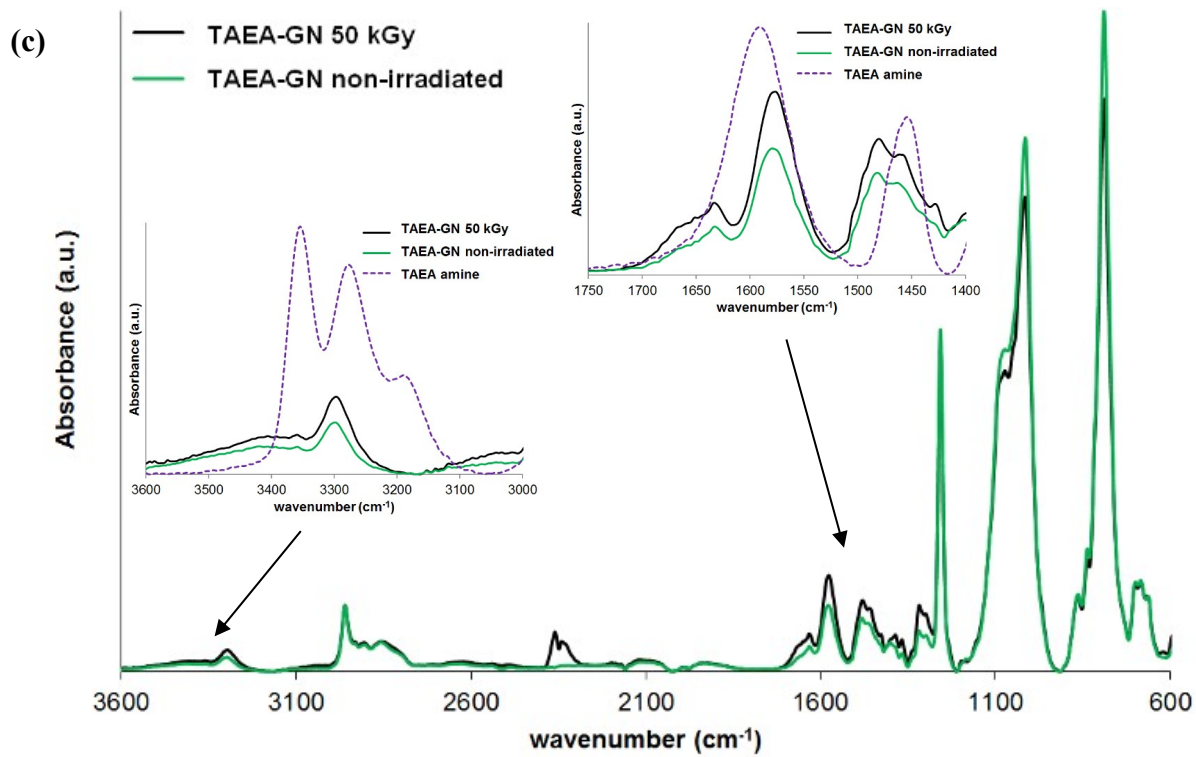
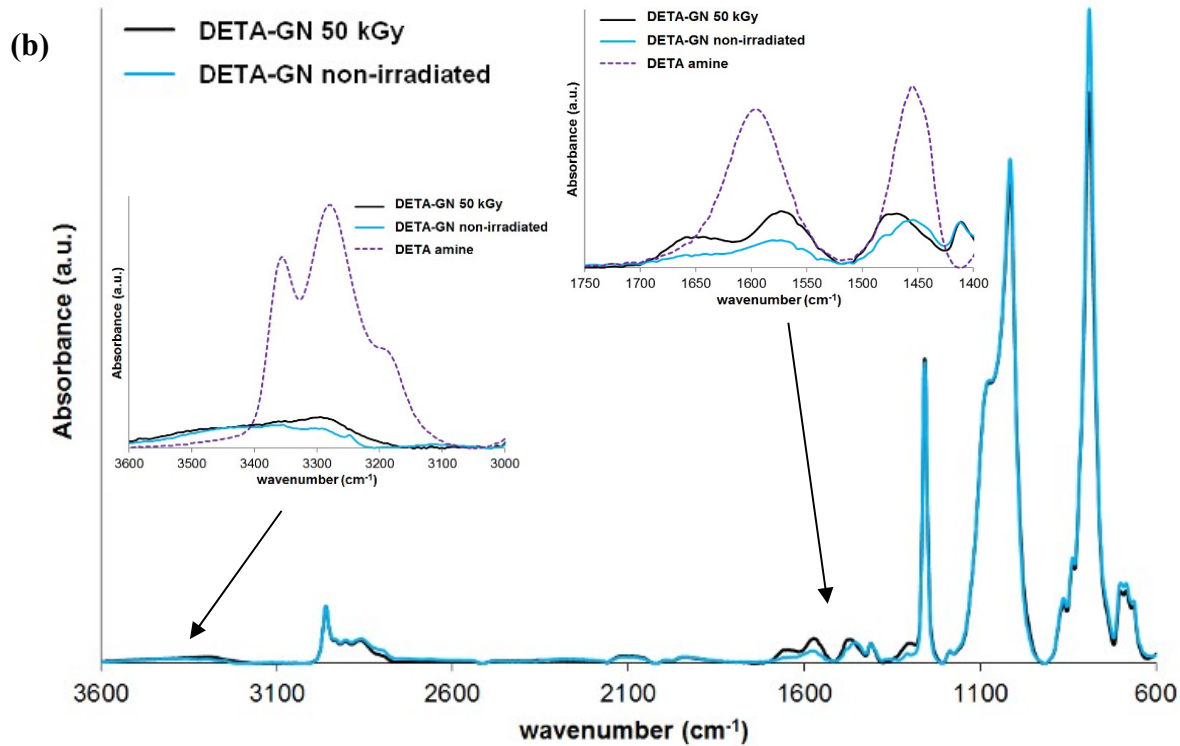
sh- shoulder, vw- very weak, w- weak, m- medium, s- strong, vs- very strong

v – stretching, δ – bending, ρ – rocking, π – wagging, τ – twisting

In case of multiple possible vibrational modes, the main is written first.

However, for assessment of the radiation effects in irradiated gel-networks epoxy absorptions were not appropriate so amine absorptions were used. In a first step of two-step preparation reaction (Fig. 2) primary amine reacts with an epoxy group and is converted into secondary amine. In the second step it may react with another epoxy group to be converted into tertiary amine. Although those absorptions between 1600 cm^{-1} and 1550 cm^{-1} are weak they provided useful information on reaction outcomes. N-H bending absorption of primary amine at 1596 cm^{-1} is seen only in FTIR spectra of pure amines (Fig. 4, inserts). No primary amine absorptions were seen in any of gel-network spectra apparently indicating that first reaction step of curing was completed. Secondary amine absorptions appeared at about 1570 cm^{-1} . Since no N-H bond exists in tertiary amine and C-N absorptions overlap with those of PDMS the changes related to second step of curing reaction could not be monitored. Taking into account relative contribution of other secondary amine groups present in amines used for curing (0 in DAP and TAEA, 1 in DETA, 2 in TETA) the extent of curing in non-irradiated gel-networks increased in order DETA < TETA < DAP < TAEA.





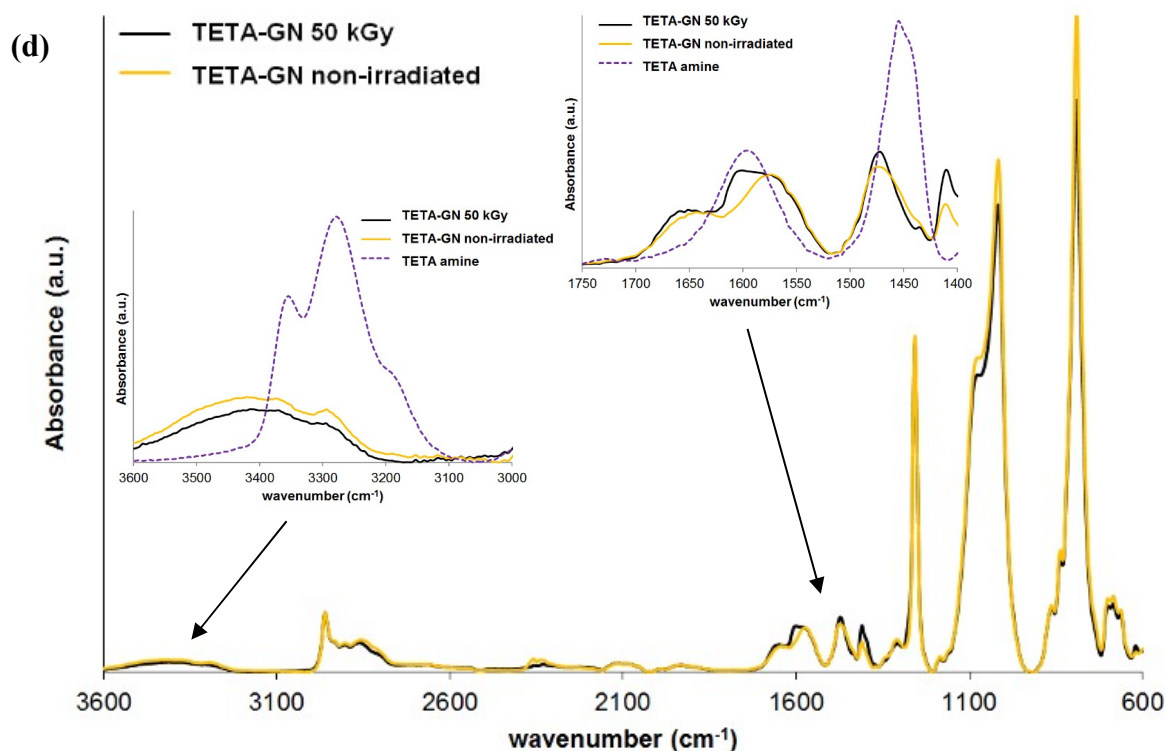


Fig. 4. ATR-FTIR spectra of non-irradiated and irradiated gel-networks: (a) DAP-cured, (b) DETA-cured, (c) TAEA-cured, (d) TETA-cured. In inserts the spectra of corresponding pure amine are shown (dashed line) for clarity.

On irradiation to $D = 50$ kGy no new absorptions that would indicate chemical changes in the gel-network were detected neither in ATR-FTIR spectra nor in Raman spectra. On the other hand the changes in secondary amine group absorptions were observed in all spectra of irradiated gel-network samples. In DETA-cured gel-network there was a relative increase of 1570 cm^{-1} FTIR absorption intensity indicating further reaction between residual primary amines and DGE took place. Since TETA amine itself contains two secondary amine groups changes due to radiation induced reaction can produce only minor effect on 1570 cm^{-1} absorption intensity so it is no surprise that none were observed. Still there is a relative intensity increase of methylene absorption at 1410 cm^{-1} that is consistent with radiation induced crosslinking as proposed by Huszank (2014). Only in the spectra of irradiated DAP-cured gel-network there was a decrease in secondary amine group intensity indicating further conversion to tertiary amine. In the spectra of irradiated TAEA-cured gel-network no clear trend was observed probably because the chance of reaction of DGE and amine group in relatively dense network formed by initial curing is low. In all irradiated gel-networks siloxane absorptions at 864 cm^{-1} and at 1015 cm^{-1} became relatively weaker relative to the corresponding methylene absorption. Since the intensities in ATR-FTIR, among else, depend on the contact between ATR crystal and the sample, that decrease may indicate that the gel-network became somewhat firmer on irradiation (Buffeteau et al., 1996). The

change of polysiloxane absorption intensity was the least in DAP-cured gel-network because due to hydrogen bonding it was firm even before irradiation.

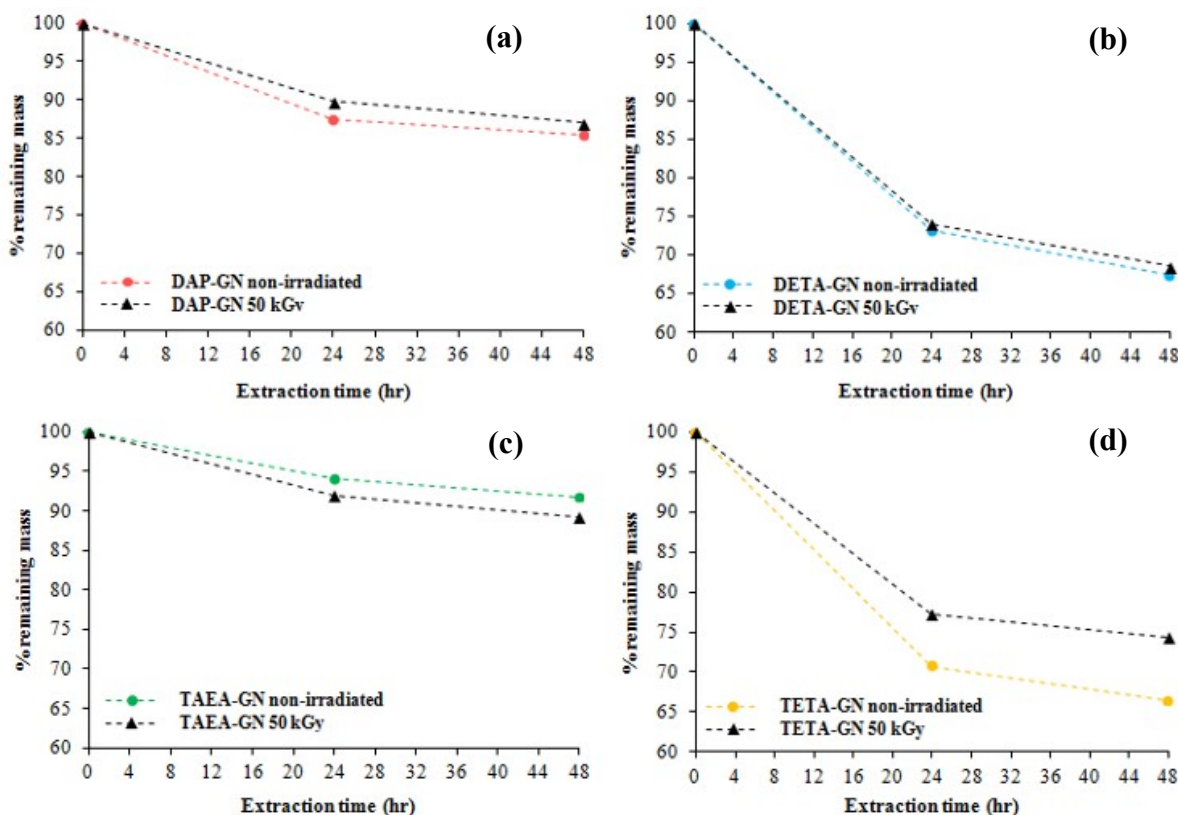


Fig. 5. Residual mass after 24 and 48 hours of Soxhlet extraction in hexane for non-irradiated and irradiated gel-networks: (a) DAP-cured, (b) DETA-cured, (c) TAEA-cured, (d) TETA-cured.

Non-irradiated gel-networks were relatively stable and their residual masses after Soxhlet extraction were above 66 % (Fig. 5, Table 3). The effect of the amine type used was again observed. The residual mass increased in order TETA ~ DETA < DAP < TAEA. The order is similar to that of the secondary amine FTIR absorption intensity increase what confirms that 1570 cm^{-1} FTIR absorption intensity is correlated to the extent of curing. It should be noted that the residual mass of TAEA- and DAP-cured gel-networks was similar and significantly higher than that of DETA- and TETA-cured ones. The change of residual mass on extraction of most of the irradiated gel-networks was so slight that it can be considered to be within the limits of the experimental error. That is consistent with results of Rogero et al. (2005) obtained on irradiation of PDMS to doses above 25 kGy. They proposed that the rigidity of previously formed network impedes the further reaction. A significant residual mass increase occurred only on extraction of irradiated TETA-cured gel-network most likely because of low extent of initial curing.

Table 3. Residual mass on Soxhlet extraction, results of swelling in *n*-hexane, AC electrical conductivity, peak temperature and enthalpy of endothermic transformation (DSC) of non-irradiated PDMS-DGE gel-networks and those irradiated to D = 50 kGy (average values of two measurements).

Sample		% remaining mass after 48 hr of Soxhlet extraction	Equilibrium swelling (%)	σ (real) (S/cm)	T _t (°C)	ΔH (Jg ⁻¹)
DAP	non-irradiated	85.42	55.83	$8.26 \cdot 10^{-11}$	110.02	9.62
	D = 50 kGy	87.03	59.38	$4.08 \cdot 10^{-10}$	107.96 121.80	35.46
DETA	non-irradiated	67.31	87.93	$2.68 \cdot 10^{-10}$	98.19	7.90
	D = 50 kGy	68.50	94.48	$2.05 \cdot 10^{-8}$	123.97	38.55
TAEA	non-irradiated	91.74	65.46	$1.05 \cdot 10^{-10}$	112.72	28.56
	D = 50 kGy	89.24	69.41	$3.17 \cdot 10^{-9}$	129.50	31.13
TETA	non-irradiated	66.45	73.90	$1.59 \cdot 10^{-8}$	91.33	8.25
	D = 50 kGy	74.32	79.79	$2.68 \cdot 10^{-8}$	116.45	62.24

Considering the amine used for curing, gel-network swelling was the lowest for DAP-cured one and increased in order DAP < TAEA < DETA < TETA and the order was unaffected by irradiation to D = 50 kGy. All samples reached equilibrium swelling after 12 hours. In gel-networks prepared with diamines swelling increased about 10% compared to non-irradiated ones. Since the capacity of gel-networks to absorb *n*-hexane increased irradiation obviously improved their properties (Palsule et al., 2008). Irradiation effect was the least in case of triamine (Table 3). The apparent firmness of the gel-networks is inversely correlated to the extent of swelling in *n*-hexane.

Electrical conductivity of polymers like PDMS is predominately ionic and is highly sensitive to changes in polymer microstructure. Thus dielectric spectroscopy gave additional insight into effects of amines used for curing of studied PDMS-based gel-networks. It is known that ionizing radiation induces charge carriers causing at least temporarily increase in conductivity. If crosslinking occurs a decrease in conductivity is expected because higher network density reduces charge transport. On the other hand degradation may ease charge movement thus increasing the conductivity. At a particular temperature the resulting conductivity reflects the extent of each of those processes, polymer properties and the irradiation dose.

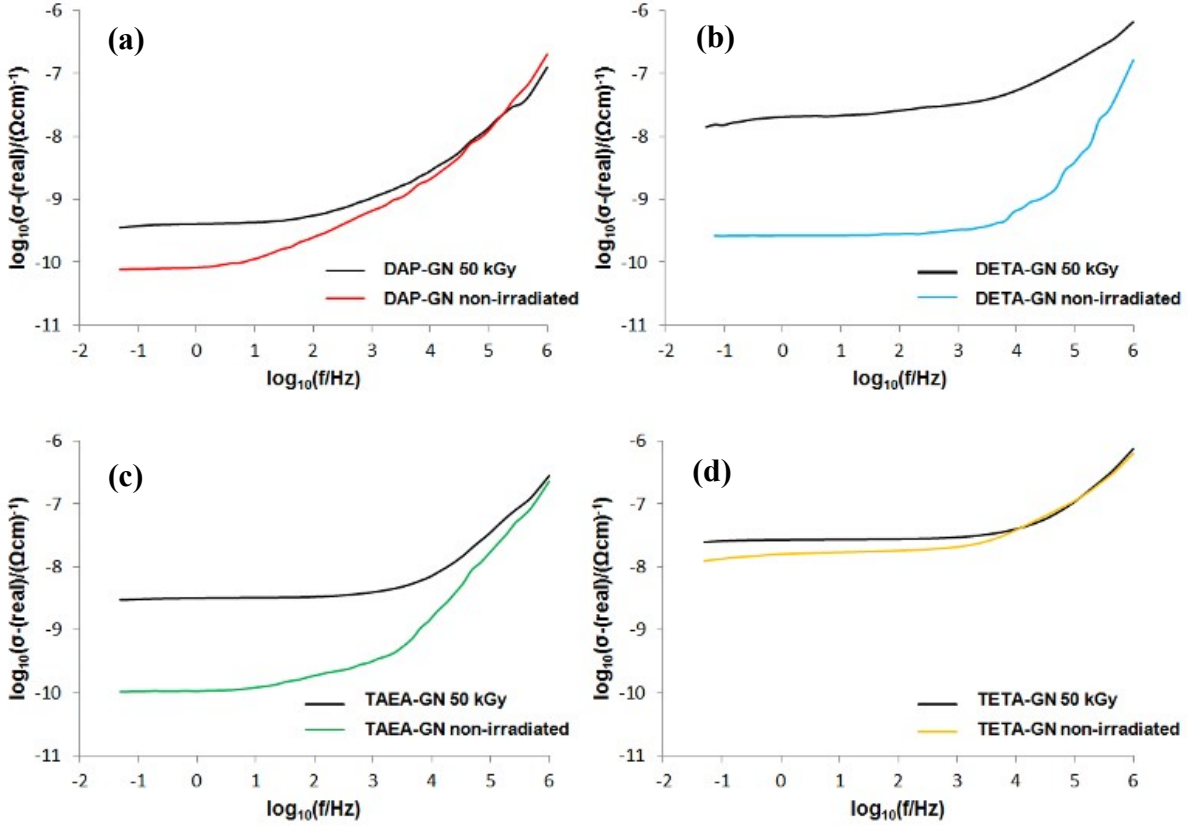


Fig. 6. AC electrical conductivity of non-irradiated and irradiated gel-networks: (a) DAP-cured, (b) DETA-cured, (c) TAEA-cured, (d) TETA-cured.

As it is common in polymers, the frequency dependence of real part of AC conductivity of studied gel-networks (Fig. 6) consists of a low-frequency plateau and a linear increase at high frequencies. Greater frequency range of conductivity plateau corresponds to greater disorder in polymer system (Papathanassiou et al., 2007). The greatest frequency range of conductivity plateau followed by the least steep increase at higher frequencies confirms the greatest disorder in TETA-cured gel-network. The frequency plateau range of DETA-cured gel-network was similar to that of TETA-cured but those of DAP- and TAEA-cured gel-networks were significantly shorter. Non-irradiated TAEA-cured gel-network displays a step in frequency dependence of conductivity that might correspond to current relaxation at the interfaces between regions of different conductivity. Such regions might arise due to an intertwined network that is much more likely when a triamine is used as a curing agent. On irradiation the width of the frequency plateaus increased indicating reduction in ordering. The increase was pronounced in TAEA-cured sample likely indicating slight degradation what is consistent with Soxhlet extraction results. Due to hydrogen bonding both the conductivity and the frequency range of its plateau are the lowest for DAP-cured gel-network.

The AC conductivity is determined as a conductivity value extrapolated to zero frequency. The lowest conductivity was that of non-irradiated DAP-cured gel-network. That is obviously due to

the hydrogen bonding as a consequence of the DAP amine hydroxy group. Similarly in TAEA-cured gel-network secondary valent interactions of multiple PDMS chains linked to a triamine reduced charge mobility. The conductivity of DETA-cured gel-network was somewhat higher than that of DAP- and TAEA-cured ones but about the same order of magnitude. Non-irradiated TETA-cured gel-network had unexpectedly high conductivity, about 2 orders of magnitude higher than the conductivity of other gel-networks. Such high conductivity is likely a result of lower extent of initial curing. The overall effect of amines on AC electrical conductivity (Table 3) of non-irradiated gel-networks prepared with them increased in order $\text{DAP} \sim \text{TAEA} < \text{DETA} < \text{TETA}$, almost inversely as did the remaining mass on Soxhlet extraction. On irradiation the conductivity of DAP-cured and particularly TETA-cured gel-networks increased very little. Since in both cases FTIR spectra revealed somewhat reduced -OH intensities (Fig. 4, inserts) changes in hydrogen bonding and/or further curing are likely cause of observed changes. On the other hand electrical conductivity of DETA-cured gel-networks increased significantly, for almost 2 orders of magnitude while conductivity of irradiated TAEA-cured one increased just slightly less. Such conductivity increase is in accordance with increased intensity of O-H band observed in FTIR spectra. Anyhow, on irradiation the effect of the amine used for gel-network curing on order of AC conductivity increase remained the same: $\text{DAP} < \text{TAEA} < \text{DETA} < \text{TETA}$.

DSC thermograms of all gel-network samples (Fig. 7) revealed an endothermic transformation resembling to a melting peak. It is not true melting because there is no corresponding exothermic transformation on cooling and it does not appear on immediate reheating. However, it reappears if the same experiment is repeated on the same sample after several days so it is not caused by residual reaction either. It is presumably a gel collapse process or volume phase transition (Shibayama, 1993). The highest gel collapse temperature is that of the TAEA-cured gel-network. Among gel-networks prepared with diamines the highest collapse temperature is of the one prepared with DAP. Gel collapse temperatures decrease in the same order as the length of reactive diamine ($\text{DAP} > \text{DETA} > \text{TETA}$). This confirms that shorter chain diamines and branched triamine form denser network. On irradiation all peak temperatures shifted to higher values. In thermogram of irradiated DAP-cured gel-network an additional sharp peak appeared at somewhat lower temperature probably due to increased hydrogen bonding. Enthalpies of endothermic transformations of all non-irradiated gel-networks prepared with diamines (DAP, DETA, TETA) were similar and about an order of magnitude lower than that of gel-network prepared with a triamine (TAEA). On irradiation enthalpies of gel-networks prepared with diamines significantly increased while in TAEA cured gel-network the increase was only slight.

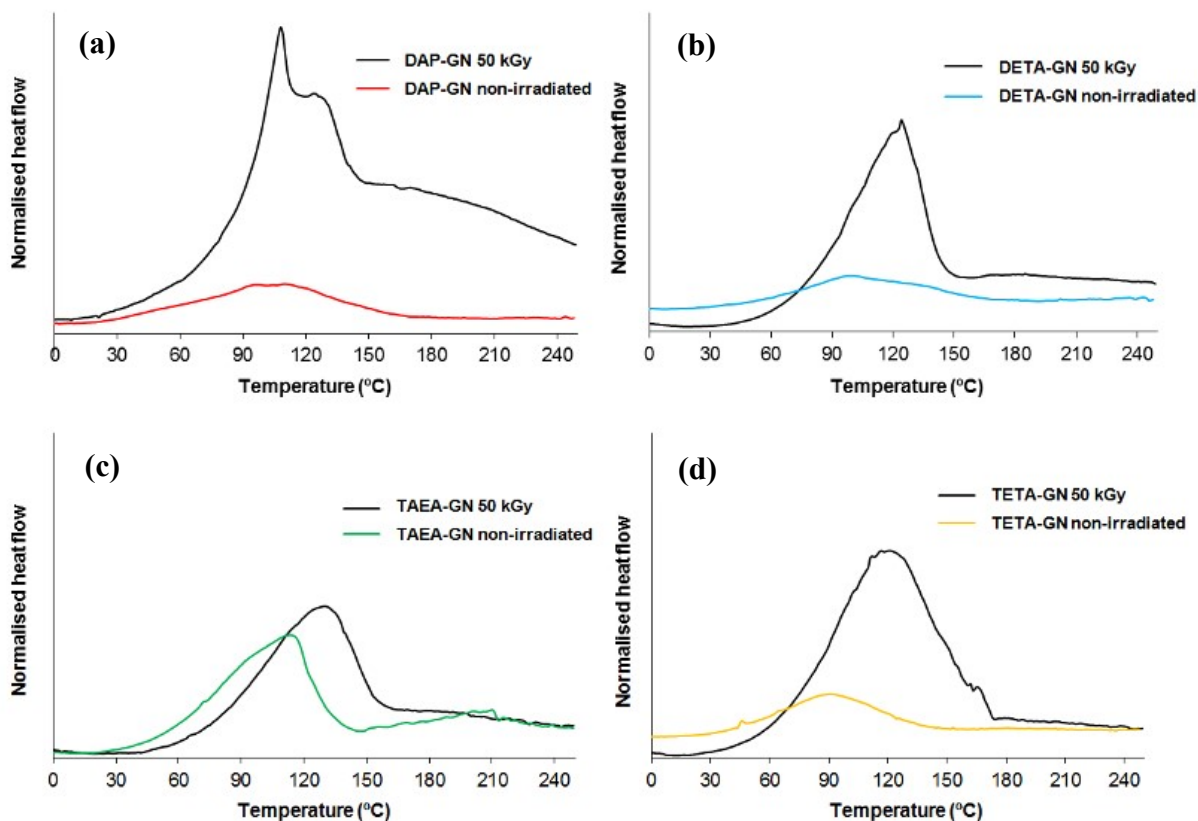


Fig. 7. DSC thermograms of non-irradiated and irradiated gel-networks: (a) DAP-cured, (b) DETA-cured, (c) TAEA-cured, (c) TETA-cured. Thermograms are normalized to sample mass.

4. CONCLUSIONS

Low temperature curing of PDMS-DGE with selected amines produced stable transparent gel-networks. While Raman spectra revealed presence of residual epoxy-group absorptions the best way to gain insight into the curing reaction extent was to monitor secondary amine absorption intensities in FTIR spectra.

Even though contribution of amine segments to PDMS-based gel-networks is relatively small their structure significantly influenced the properties of studied PDMS-based gel-networks. The most important property of an amine that impacted gel-networks properties was the ability to form hydrogen bonds, in case of DAP, or produce denser network like TAEA, a triamine. However there were also significant differences in properties of gel-networks prepared with mutually similar diamines DETA and TETA that can be considered a dimer and a trimer of ethylenediamine.

In the studied gel-networks there is a complex interaction of extent of initial curing that depended on the amine used and the resulting (dis)order that strongly influenced the outcome of irradiation to $D = 50$ kGy. The temperature of an endothermic transition presumably caused by reversible gel-network collapse that was observed in DSC thermograms of all gel-networks depended on the amine type and shifted to higher values on irradiation. Changes in most properties like residual

gel content on extraction or AC electrical conductivity and its frequency dependence were more pronounced in gel-networks prepared with diamines DETA and TETA than in those prepared with amines capable of significant secondary valent interactions (DAP and TAEA). Radiation curing and/or crosslinking seem to have occurred only in TETA-cured gel-network and it was mostly due to lower extent of initial reaction. Since swelling of gel-networks increased it may be concluded that irradiation improved their properties.

References

1. Brockmeyer, B., Kraus, U. R., Theobald, N., 2015. Accelerated solvent extraction (ASE) for purification and extraction of silicone passive samplers used for the monitoring of organic pollutants. *Environ. Sci. Pollut. Res.* 22, 19887-19895.
2. Buffeteau, T., Desbat, B., Eyquem, D., 1996. Attenuated total reflection Fourier transform infrared microspectroscopy: Theory and application to polymer samples. *Vib. Spectrosc.* 11, 29-36.
3. Cai, D., Neyer, A., Kuckuk, R., Heise, H. M., 2010. Raman, mid-infrared, near-infrared and ultraviolet–visible spectroscopy of PDMS silicone rubber for characterization of polymer optical waveguide materials. *J. Mol. Struct.* 976, 274-281.
4. De Deene, Y., Hill, R., Skyt, P. S, Booth, J., 2015. Flexydos3D: A new deformable anthropomorphic 3D dosimeter readout with optical CT scanning. *J. Phys. Conf. Ser.* 573, 012025. - doi:10.1088/1742-6596/573/1/012025
5. Djouani, F., Zahra, Y., Fayolle, B., Kuntz, M., Verdu, J., 2014. Degradation of epoxy coatings under gamma irradiation. *Radiat. Phys. Chem.* 82, 54-62.
6. Hill, D. J. T., Preston, C. M. L., Salisbury, D. J., Whittaker, A. K., 2001. Molecular weight changes and scission and crosslinking in poly(dimethyl siloxane) on gamma radiolysis. *Radiat. Phys. Chem.* 62, 11-17.
7. Huszank, R., 2014. Irradiation Induced Chemical and Physical Effects in Silicones, in: A. Tiwari, M. D. Soucek (Eds.), *Concise Encyclopedia of High Performance Silicones*, 1st edition, Wiley - Scrivener Publishing, New Jersey, pp. 75-84.
8. Jones, R. G., Kahovec, J., Stepto, R., Wilks, E. S., Hess, M., Kitayama, T., Metanomski, W. V., 2009. *IUPAC: Compendium of Polymer Terminology and Nomenclature*, RSCPublishing, Cambridge, pp. 211-236.
9. Liu, J., Zheng, X. J., Tang, K. Y., 2013. Study on the Gravimetric Measurement of the swelling behaviors of polymer films, *Rev. Adv. Mater. Sci.* 33, 452-458.
10. Mark, J. E., 2004. Some interesting things about polysiloxanes. *Acc. Chem. Res.* 37, 946-953.

11. Palsule, A. S., Clarson, S. J., Widenhouse, C. W., 2008. Gamma irradiation of silicones. *J. Inorg. Organomet. Polym.* 18, 207-221.
12. Papathanassiou, A. N., Sakellis, I., Grammatikakis, J., 2007. Universal frequency-dependent AC conductivity of conducting polymer networks. *Appl. Phys. Lett.* 91, 122911.
13. Petrie, E. M., 2006. *Epoxy Adhesive Formulations*, McGraw-Hill, New York, pp. 85-110, 203-226.
14. Socrates G., 2001. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, 1st edition, John Wiley & Sons, Chichester, pp. 107-113, 241-246.
15. Rogero, S. O., Sousa, J. S., Alario Jr., D., Lopergolo, L., Lugao, A. B., 2005. Silicone crosslinked by ionizing radiation as potential polymeric matrix for drug delivery, *Nucl. Instrum. Methods Phys. Res., Sect. B* 236, 521-525.
16. Rogovina, L. Z., Vasil'ev, V. G., Braudo E. E., 2008, Definition of the Concept of Polymer Gel, *Polym. Sci. Ser. C*, 50, 85-92.
17. Shibayama, V., Tanaka, T., 1993. Volume phase transition and related phenomena of polymer gels. *Adv. Polym. Sci.* 109, 1-62.
18. Yamauchi, A., 2001. Gels: Introduction, in: Y. Osada, K. Kajiwara (Eds.), *Gels Handbook Volume 1: The Fundamentals*, Academic Press, San Diego, pp. 7-19.